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DIFFERENTIAL INFRARED SPECTROMETRY TECHNIQUE USED FOR THE STUDY OF COALS

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ABSTRACT

For the technique described in this paper, two specimens of coal were prepared for runs in the infrared double beam spectrometer. One specimen was prepared for the coal as received from the mine and this was placed in the reference beam. The other sample was prepared from coal which had been heated in a pressure-tight container to the softening temperature. This was placed in the sample beam. The differential infrared spectrometer pattern thus obtained enables one to observe the changes in the chemical bonds of coal which may be detected in the infrared range. Most of the tests were conducted with a coal used for blending in the coking process because of its high fluidity.

The coal samples were prepared by grinding and then casting in a potassium iodide plate.

Samples from coke buttons made from this coal were run in the infrared spectrometer and x-ray diffraction patterns were obtained from these coke samples also. In addition to this some infrared spectra were run on this coal heated in a closed crucible to various temperatures in the softening range.

The results of these tests show positive and negative changes in almost all of the spectral band assignments for coals. Data obtained from the use of this technique should provide valuable information for use in the study of coal coking mechanism.

This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-28. Reproduction in whole or in part is permitted for any purpose of the United States Government.

Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
New York City Meeting, Sept. 8-13, 1957

INFRARED SPECTROPHOTOMETRIC STUDY OF THE COKING OF COAL

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In order to understand fully the coking mechanism one must trace the chemical changes which occur as the coal undergoes the change from coal to coke. The technique described in this paper provides a means for a more precise study of the chemical changes which occur in coal, particularly those changes which occur in the coal as it is heated to the softening or fluid range. Fluidity is a key factor in the coking mechanism as evidenced by the rather good correlation of coke quality predictibility from free swelling and plastometer tests and more recently by the work of Dryden and Panchurst[1]. In the latter case a chloroform soluble product was found in the softening temperature range which proved to be a significant factor in the coking process.

Coal specimens were prepared for evaluation by means of infrared spectrophotometry. The samples were ground to a very fine powder and then thoroughly mixed in carefully weighed proportions with potassium iodide. (usually 6 mg coal per gram KI) A measured quantity of this mixture was then pressed in an evacuated die into plates for examination. The reliability of this technique has been well established in other systems[2,3,4]. Infrared spectra were obtained using a Perkin Elmer Model 21 double beam recording spectrophotometer.

The coal used for most of the tests was a blending coal used in coke ovens.* The physical properties of this coal are shown in Table I. One sample was prepared from the coal as received from the mine. The other sample of coal was heated in a pressure tight container to the fluid range; this required approximately 20 minutes. The temperature in the fluid range was held for periods of time from 10 to 30 minutes. The sample was then quenched and prepared as previously described.

The plate containing the untreated coal was placed in the reference beam of the spectrophotometer and the plate containing the coal which had been heated was placed in the sample beam. A differential absorption spectra was thus obtained. A typical pattern obtained by this method is shown in Figure 1.

Discussion of Data

Most of the spectral assignments have been made in previous studies.[5,6] Table II lists the spectral assignments used in this study. Since the coal sample which had been heated was placed in the sample beam, peaks downward on the pattern indicated vibrational spectra for bonds greater in number in the heated coal and peaks upward indicated the presence of a greater number of bonds in the untreated coal sample. Increases were noted in the 2.7 to 3 μ range (OH stretching), 3.3 to 3.4μ (aromatic hydrocarbon), 7.25μ (hydrocarbon

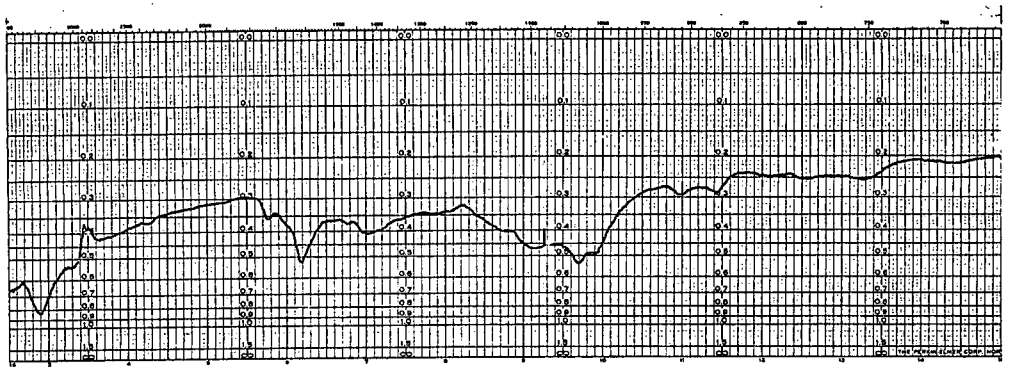
* Coal samples were obtained from the Columbia-Geneva Steel Division, U. S. Steel Corporation.

Table I. Physical Properties of Coal Used in Differential Infrared Spectrophotometer Tests

Proximate Analysis		Ultimate Analysis		Gieseler Type Plastometer	
H_2O	2.94	C	75.20	Initial Soften. Temp.	341°C
V. M.	30.53	H_2	5.23	Max. Fluidity Temp.	422°C
F. C.	58.17	N_2	1.63	Max. Dial Div./Min.	2,977
Ash	11.30	Ash	11.30	Solidification Temp.	469°C
Sulfur	0.82	S	0.82		
		O_2	5.82		

Table II. Spectral Assignments for Coal

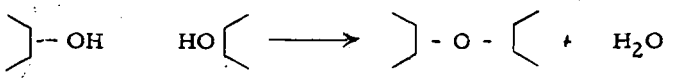
Microns	
3.00	Hydrogen-bonded OH or NH (see discussion in text)
3.30	Aromatic CH, weak
3.42 3.49	Naphthenic and/or aliphatic CH bonds
5.87	C=O band, weak shoulder
6.19	Very intense band; may be partly caused by a conjugated carbonyl structure such as in quinones.
6.90	CH_2 groups
7.25	CH_3 groups
9.67	Aromatic band, intense in aromatic ethers



WAVELENGTH IN MICRONS

Figure 1. Differential infrared spectrophotometric pattern. Untreated coal in the reference beam; coal heated to the softening range in the sample beam.

bending, CH_3) and 9.67μ (aromatic ethers). The increases in aromatic ether bonds suggest the following mechanism.



Other studies[7] show that coal is primarily composed of condensed aromatic rings. Experimental work discussed later in this paper and by others[8] indicates that the final coke satisfies these edge valences with C-C linkages. This suggested mechanism is based on the theory that heating coal is a continuous change of edge groups and edge bonds of these rings. Some hydrogen would of course be available from the decomposition of the CH groups. An aromatic ether could be a fluid in the softening temperature range. The action of this fluid could provide greater mobility for the rings or, perhaps, provide a surface pressure as it decomposes. Either or both of these actions could make a greater number of C-C bonds and consequently a stronger coke.

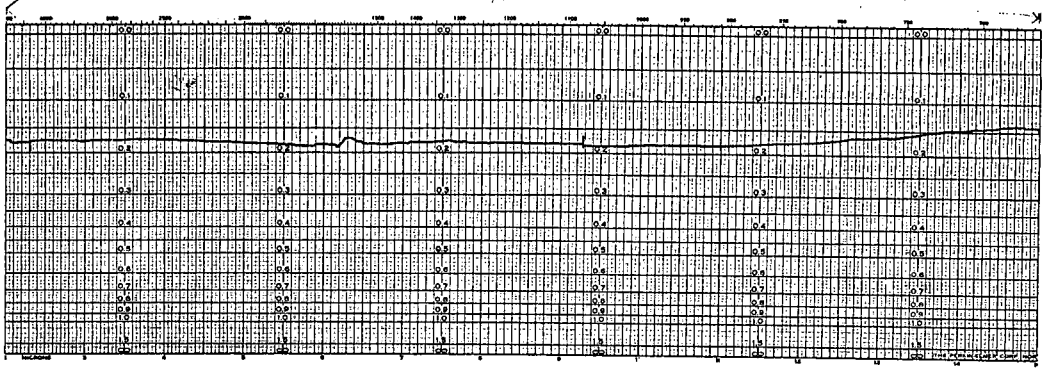
The increase in the aromatic (3.3μ - 3.4μ) bond substantiates the general theories of the coking mechanism which suggest changes to the aromatic and ultimately to a graphitic structure. There does not seem to be any ready explanation for the increase in the CH_3 band. This, too, may represent a change in edge groups. The CH_2 band shows a decrease. The 5.87μ (C=O) and the 6.19μ (C=O-quininoid) bands are shown to increase; however, some of the tests indicated a decrease. It would seem most probable that the C=O band does decrease, however the possibilities of H_2O also contributing to one of these bands (6.19μ) and of possible oxidation of the sample after removal from the container seems the best explanation for the behavior of these bands. No attempt was made to interpret bands of wave lengths greater than 9.67μ except to note their general increase, again substantiating the polymerization-graphitization theory.

To prove the reliability of the differential spectrophotometer method, two samples of untreated coal were prepared and one was placed in the reference beam and the other placed in the sample beams. The pattern obtained is shown in Figure 2.

This substantiated the reliability of the differential technique and the data obtained from it.

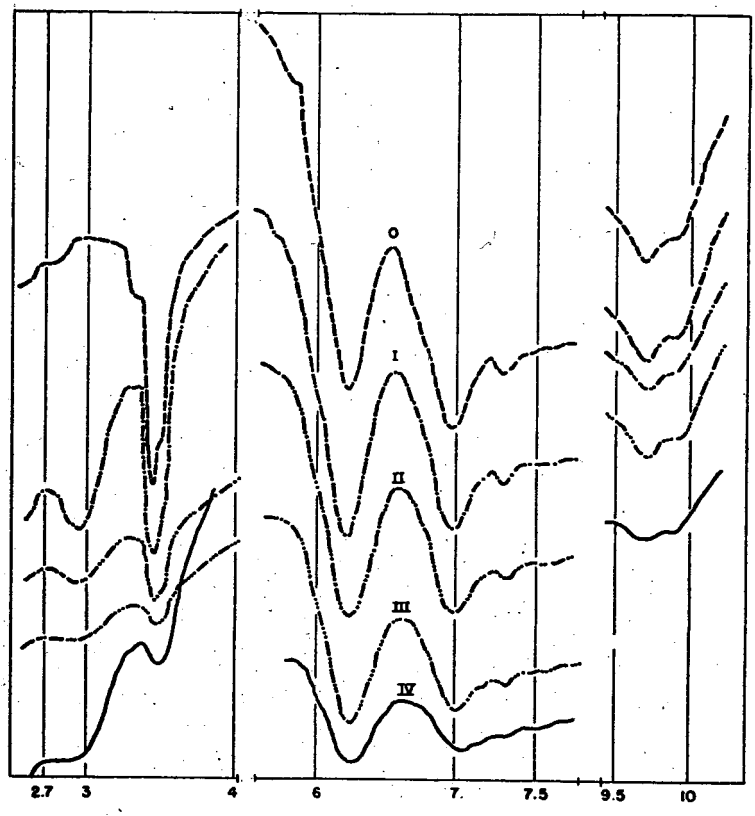
Other tests were run in a closed crucible heated rather quickly to temperatures in the fluid range. Samples were prepared as before and were run against a blank of KI in the reference beam. Figure 3 shows the results of these tests. Here the general decrease in the bands assigned to typical edge groups is noted. One should call attention, however, to the tendency for the OH and aromatic ether groups to increase before finally decreasing at the higher temperatures.

The two techniques differ, of course, in that in the second method the decomposition materials are allowed to escape. It is felt that the first (pressure-tight container) method is a more powerful tool for the study of



WAVELENGTH IN MICRONS

Figure 2. Differential infrared spectrophotometric pattern to prove technique. Untreated coal from the same sample in both the reference and sample beams.



---0 - Furnace at 500°F, coal sample 1 gram ---II - In furnace 2 minutes
---I - In furnace 1 minutes ---III - In furnace 3 minutes
—IV - In furnace 5 minutes (max. coal temperature approximately 475°C.

Figure 3. Infrared spectrophotometric pattern of coals heated in a closed crucible.

the softening stage because it provides a means for examining the bonds as they occurred in that stage before subsequent decomposition.

Samples prepared from coke buttons made from this coal were run on the infrared and in the x-ray diffraction camera. In the infrared the sample showed a very high background but a reliable pattern was obtained using 3 mg of sample in a 1 g plate. The pattern showed no indication of bands, indicating the edge groups are completely decomposed. The x-ray pattern showed a graphitic structure.

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